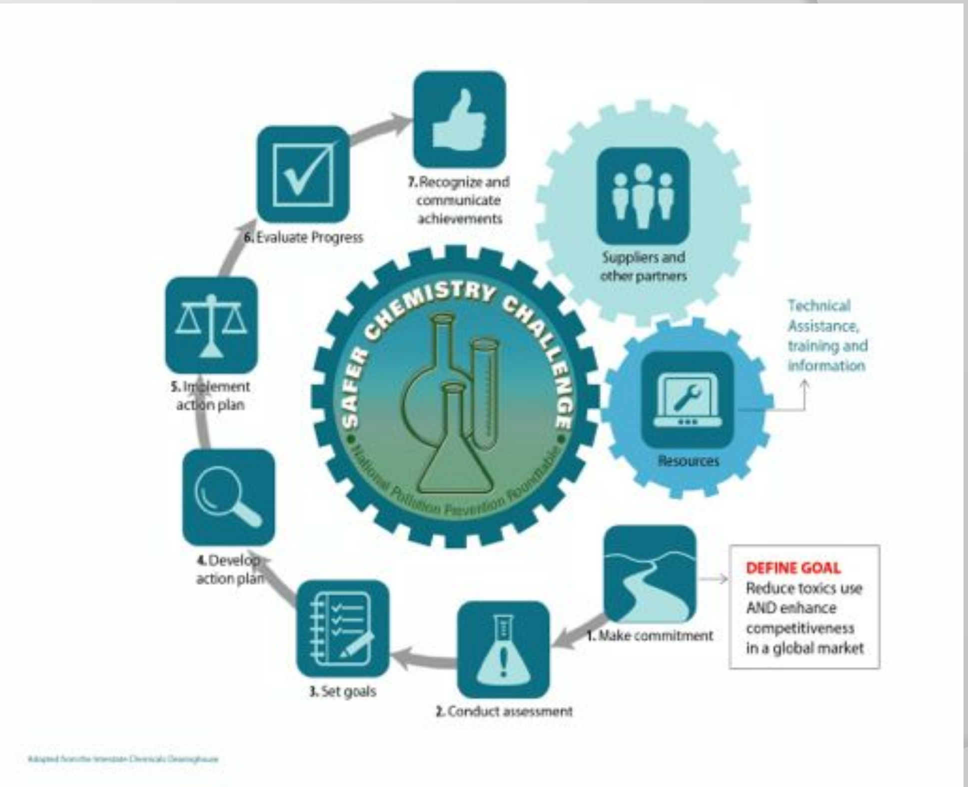
2025 SAFER CHEMISTRY CHALLENGE PROGRAM

Presented by the National Pollution Prevention Roundtable

www.p2.org/category/challenge/

2025 Safer Chemistry Challenge Program

The Safer Chemistry Challenge Program is designed to motivate, challenge, assist, and recognize companies as they identify safer alternatives to the use of toxic chemicals of concern to human health and the environment.



To sign up! www.p2.org/category/challenge/

Just Released: NPPR Chemicals Policy Report

State Chemicals Policy: Trends and Profiles

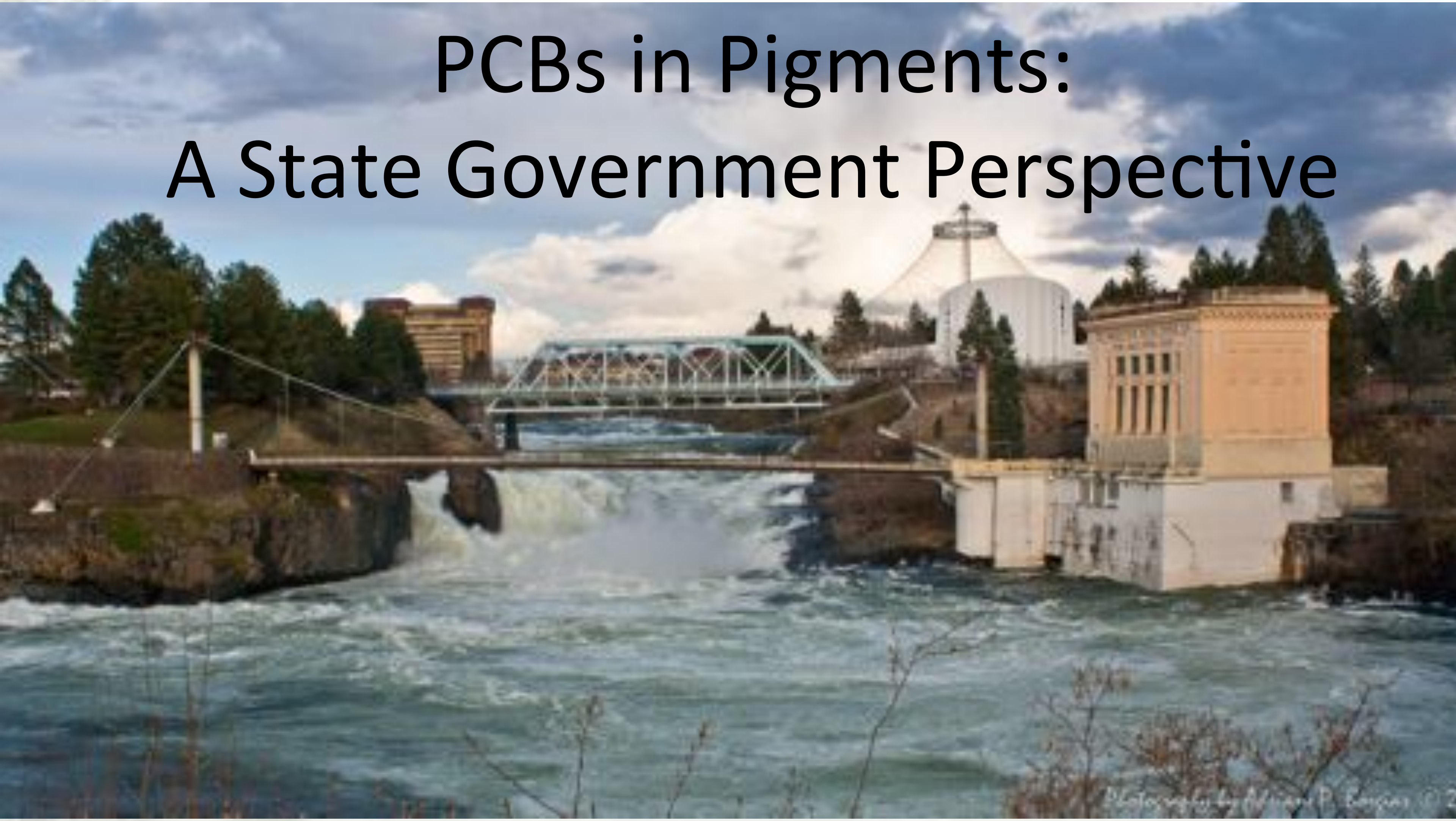
- Describes recent state legislative and policy efforts to prevent hazards and risks associated with toxic chemicals, or chemicals of concern.
- Highlights state actions to advance needed reforms of federal chemicals policy.

http://www.p2.org/wp-content/uploads/2013-state-toxics-policy-profiles-report-2.pdf

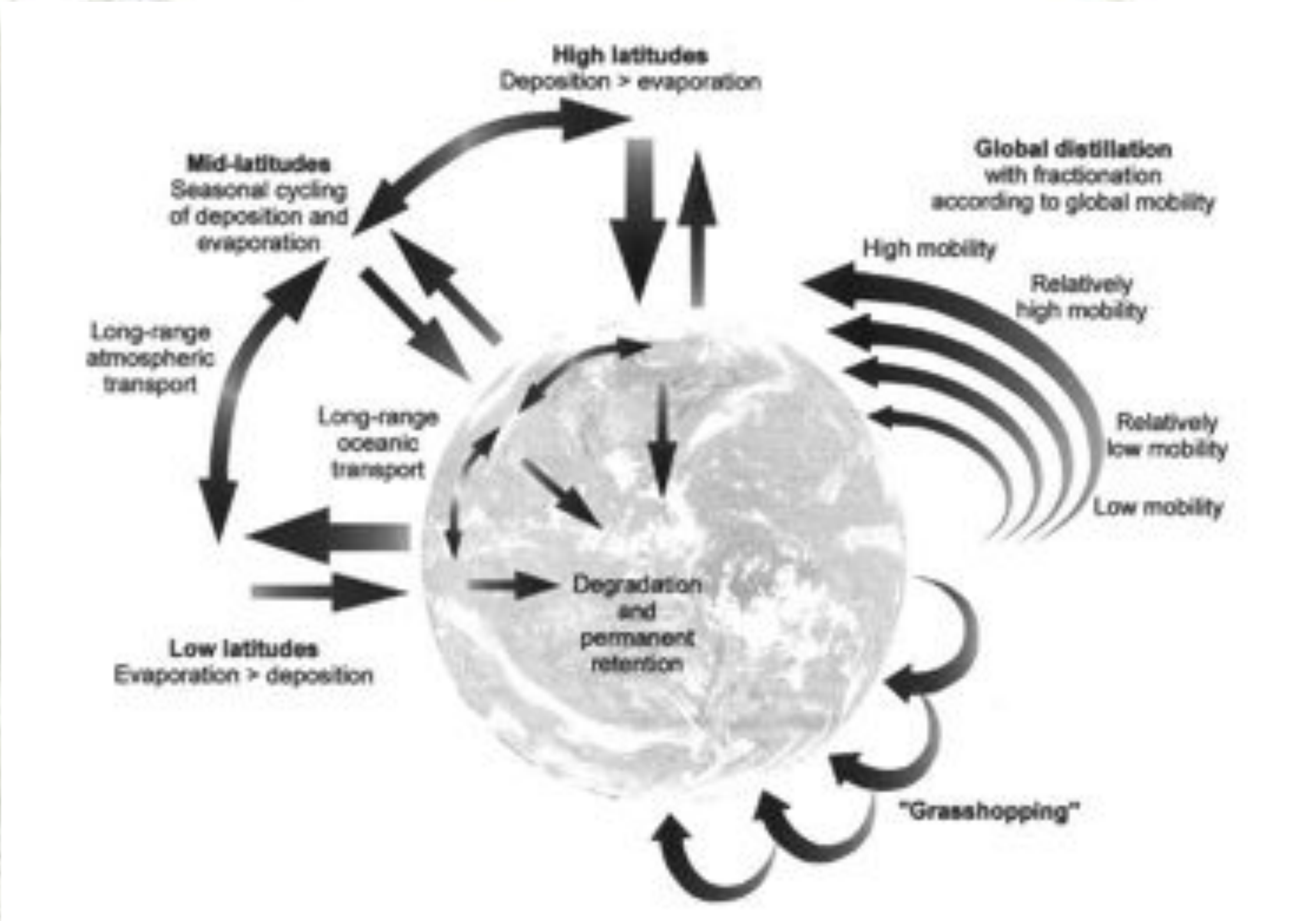
Upcoming Events

- September 25-26, 2013: GreenScreen training with Indiana and NPPR Pollution Prevention Conference
- Late October: GreenScreen training workshop, Buffalo, NY

PCBs in Pigments:
A State Government Perspective

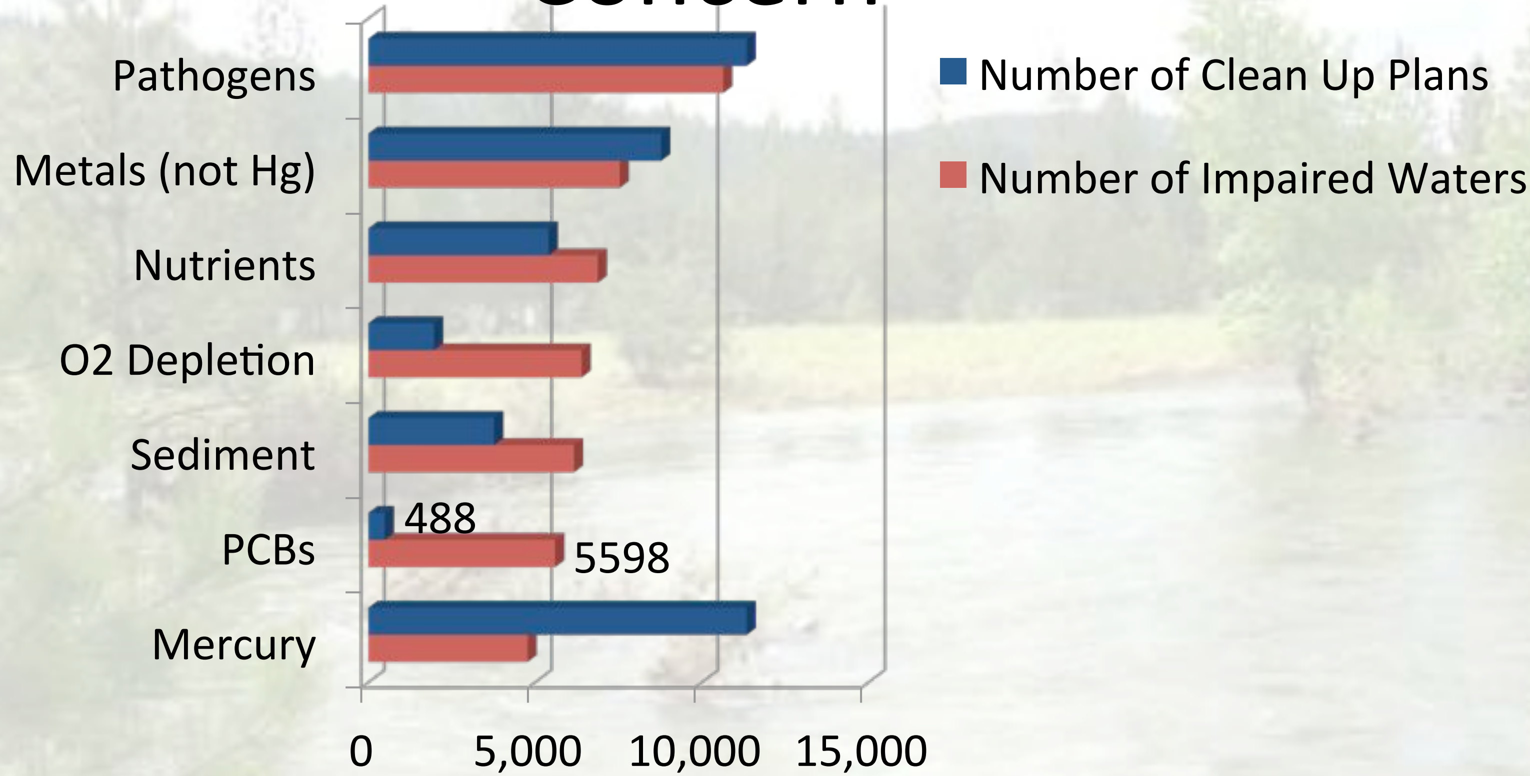


PCB: The Global View



http://www.htap.org/meetings/2008/2008_04/Presentations/09-04-08/eckhardt_htap2008.pdf

PCB: A National Water Quality Concern



EPA Watershed Assessment, Tracking and Environmental Database

- Less than 10% of water bodies impaired for PCB have clean up plans.
- PCB is generally addressed as a *legacy* issue.
- More than 200 processes that legally generate PCB.

“We don’t know where it comes from”

- **Myth:** PCB is no longer manufactured
- **Fact:** PCB is allowed as an inadvertent contaminant.

- **Myth:** A product designated as “PCB-free” has no PCBs
- **Fact:** A product can contain up to 50 ppm PCB and can be categorized as “PCB-free”

- **Myth:** The PCB in the environment is from a legacy of bad management practices.
- **Fact:** PCB continues to be produced and enters the environment through everyday use.

Telling an accurate story is essential to solving the problem.

The Spokane River

The watershed:
- 112 miles from Lake Coeur d'Alene to Columbia River
- 2,295 mi^2 in Washington
- 4,345 mi^2 in Idaho
- Of interest to 3 Tribes
- Connected with the aquifer

Development:
- Legacy mining issues
- Urbanized area primarily in Washington
- 6 hydroelectric dams
- 6 municipal permittees
- 2 industrial permittees

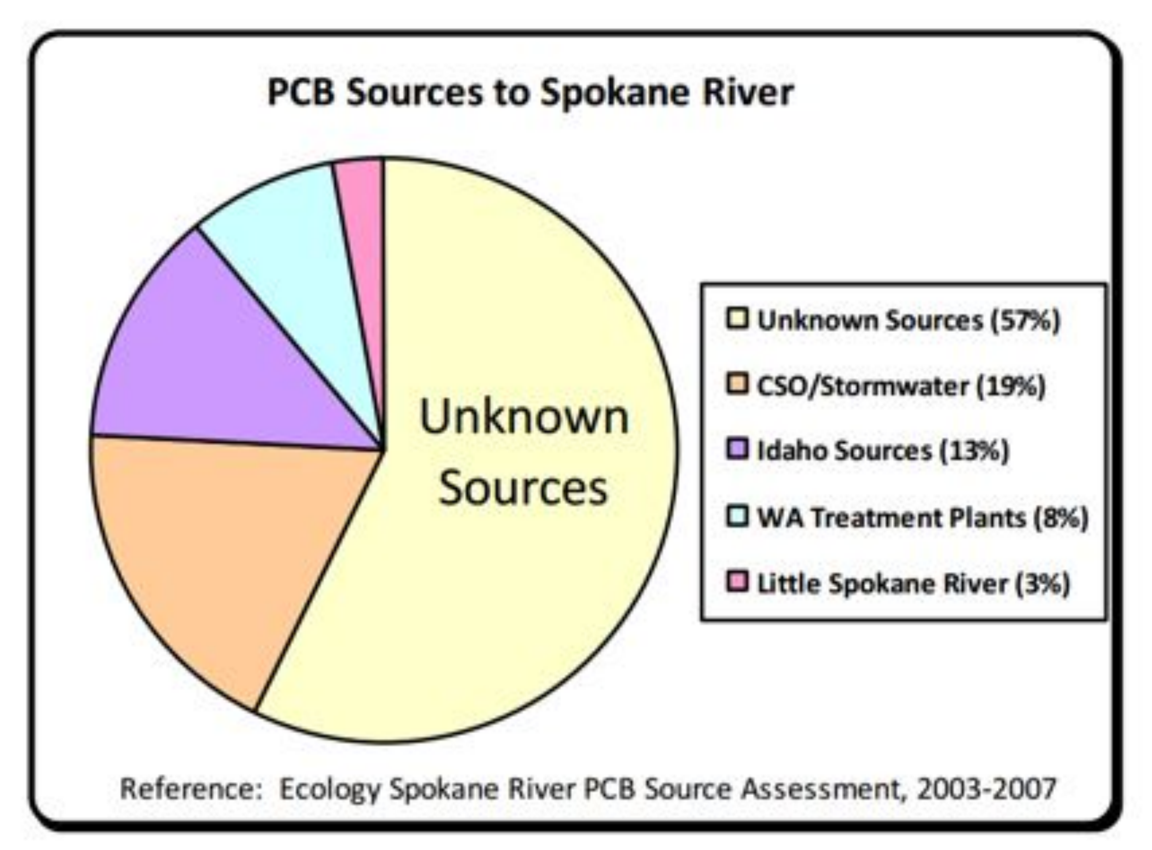
Water Quality Goals

Spokane River does not meet the Water Quality Goal for PCB

- Highest levels of PCB in state
- Fish consumption advisories since 2002
- The Spokane Tribe's 3.37 ppq is the strictest water quality standard in the state
- 98% reduction needed

In Washington 15% of "background" samples exceed the state WQS of 170 ppq

Where Does it Come From?

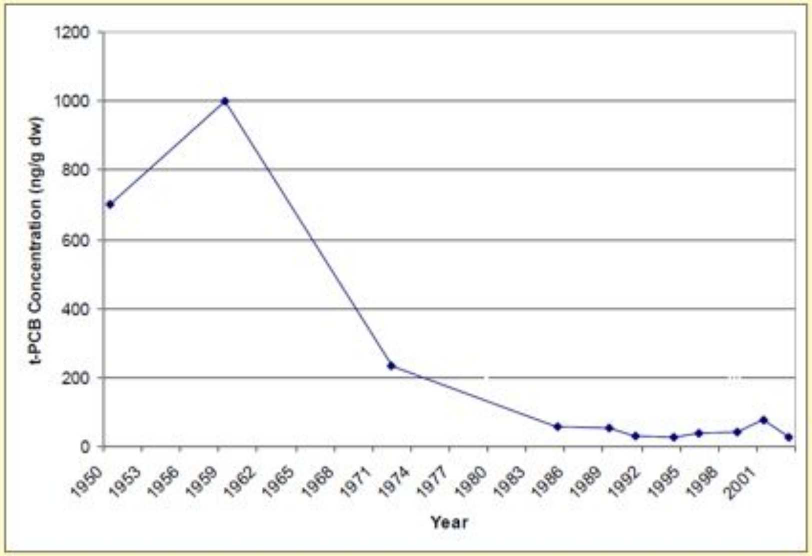


57% of the sources of PCB to the river are unaccounted for due to:

- Uncertainty of the Assessment methodology
- Lack of information about PCB in the watershed

One facility, a paper recycler, has identified pigments as a significant source of PCB in its feedstock and waste water.

The Challenge



Total PCBs in Age Dated Sediment Core (2003)

- Steep declines from 1960s through mid-1980s
- Approximately 50% decline in 20 years (1980-2000)

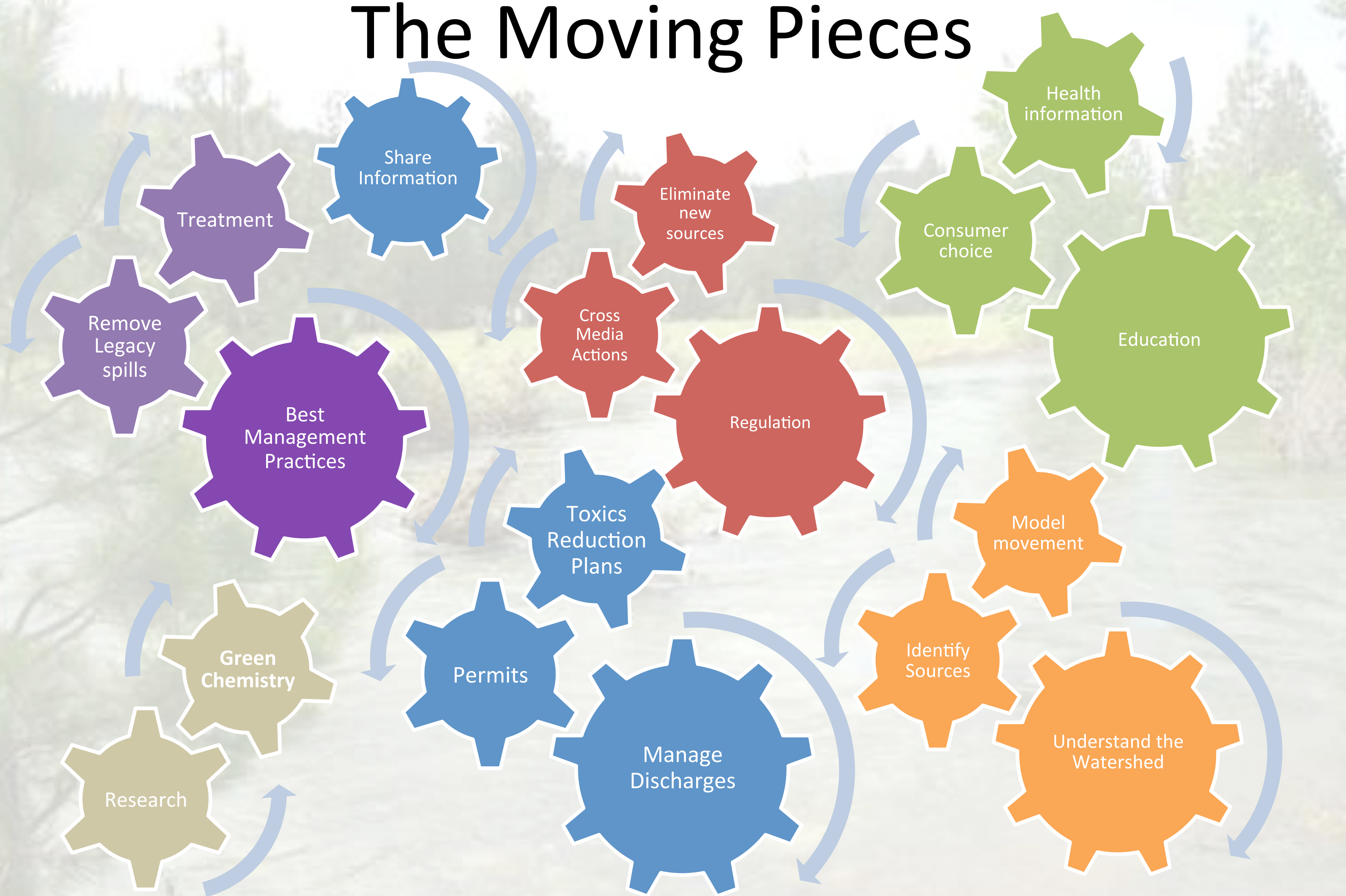
Norton, *Human Health Criteria Policy Forum,* February 8th, 2013.

- Substantial PCB reductions have been made since 1979
- More action is needed to achieve the water quality standard.

In a nutshell, we need to address all of these aspects:

- Don't make it
- Don't use it
- Use less of it
- Manage it properly
- Dispose of it properly
- End of pipe treatment

The Moving Pieces



Don’t Make It

- PCBs are produced in discrete processes but used globally
- **Can reach the environment through normal use**
- PCB contaminants affect major recycling industries
  - Paper
  - Plastics, electronics
  - Automobile recycling

Why Green Chemistry is Needed

- Color has important psychological, social, and biological significance
- Green Chemistry can
  - Provide for industry cross sector collaboration
  - Incubate new business that use a cradle-to-cradle approach
  - Create new safer, **and** environmentally benign pigments

http://www.ecy.wa.gov/toxics/docs/trs_ToxicsPolicyReformWA.pdf

For More Information

Washington State Department of Ecology

Adriane Borgias
Spokane River Water Quality Lead
(509) 329-3551
ABOR461@ecy.wa.gov

Spokane River Regional Toxics Task Force

www.srrttf.org

RUTGERS

THE STATE UNIVERSITY OF NEW JERSEY

PCBs in pigments, inks, and dyes: Documenting the problem

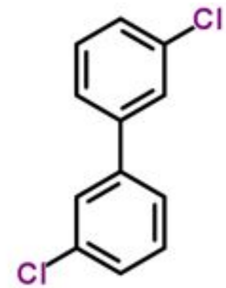
Jia Guo, Pornsawai Praipipat,
and Lisa A. Rodenburg

Department of Environmental Sciences
School of Environmental and Biological Sciences
Rutgers, the State University of New Jersey

June 19, 2013

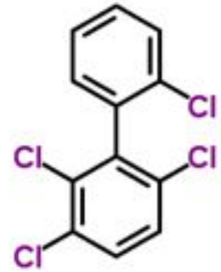
Known inadvertent PCB sources

- Organic pigments, especially diarylide yellow, produce primarily PCB 11, among others



- Titanium dioxide (inorganic white pigment) produces PCBs 206, 208, and 209

- Silicone rubber tubing produces PCBs 44 and 45, among others (don’t use for PCB sampling!)



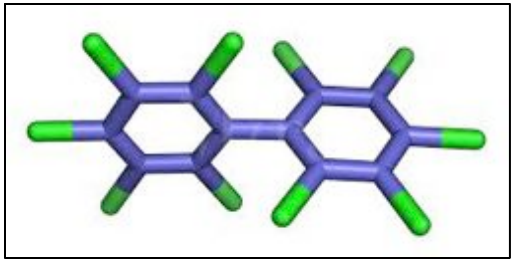
PCBs 206, 208, 209

Produced inadvertently during the making of titanium tetrachloride

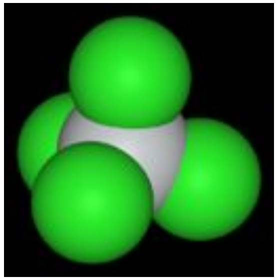
Often sold to water treatment plants as a flocculant

$$2\ FeTiO_3 + 7\ Cl_2 + 6\ C \rightarrow 2\ TiCl_4 + 2\ FeCl_3 + 6\ CO$$

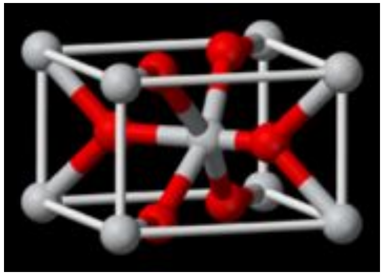
This carbon is chlorinated to form PCBs



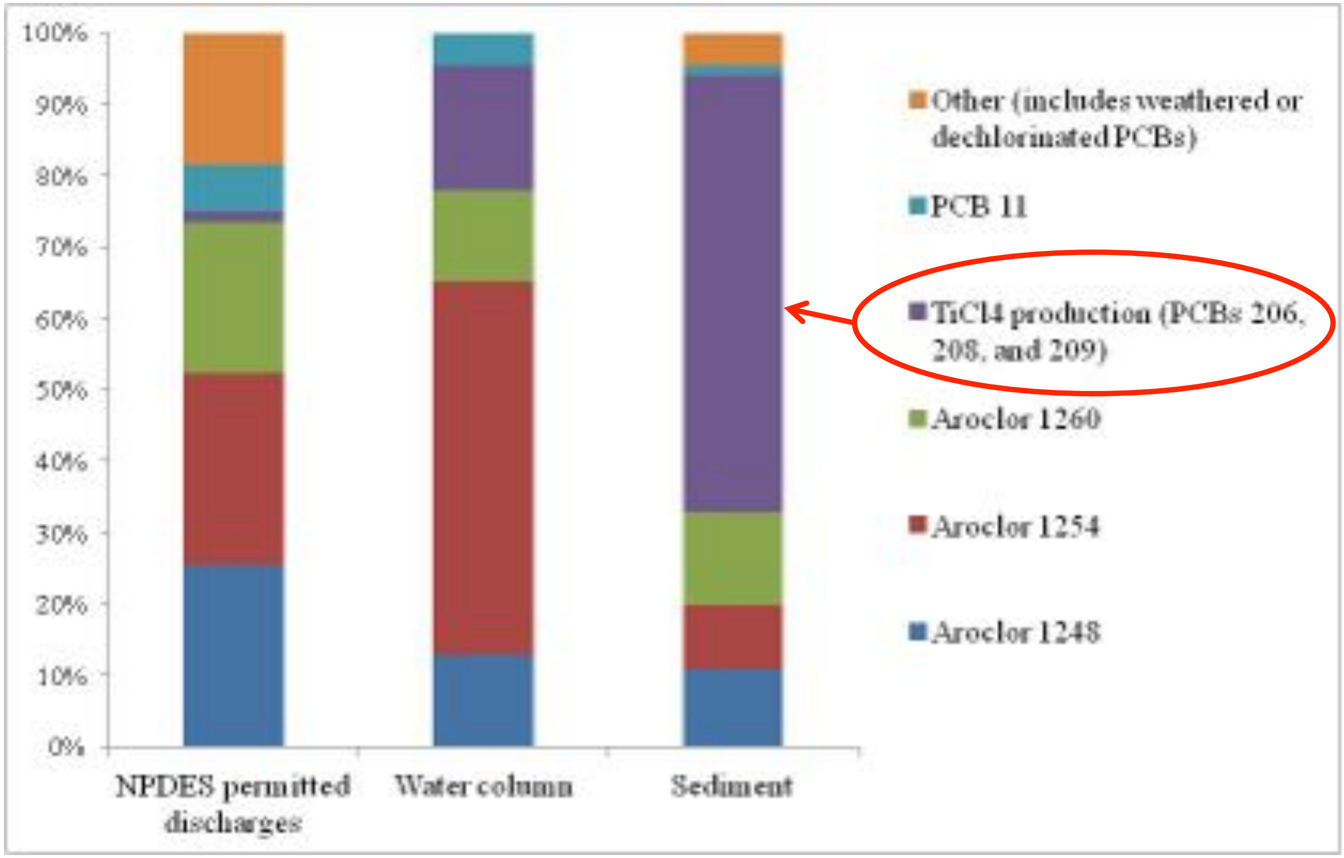
Most $TiCl_4$ is then used to make TiO_2 (white pigment)



$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

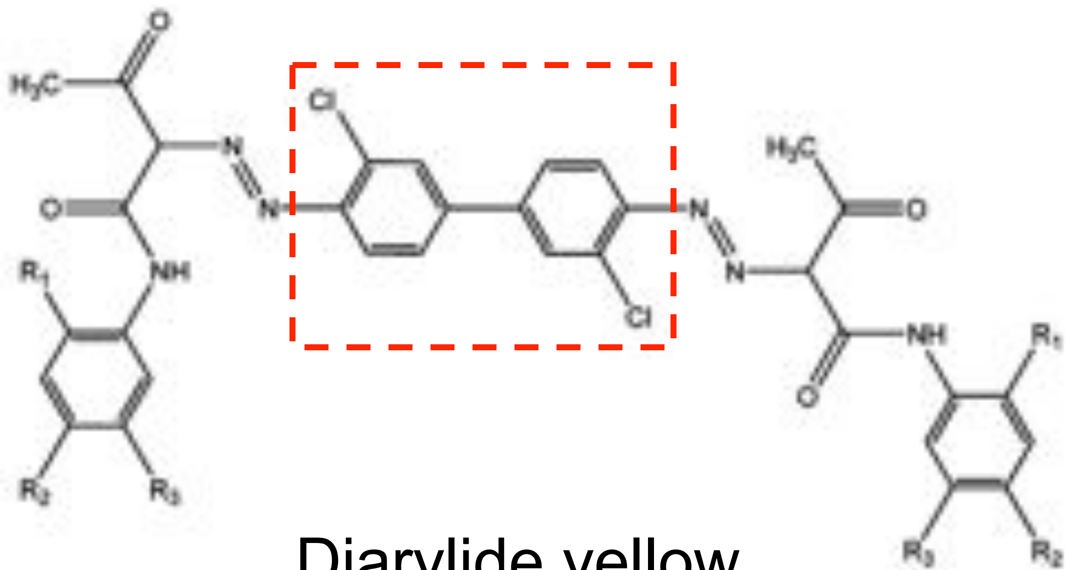


PCBs from TiO_2 production in Wilmington, DE, contribute 61% of all PCBs in surface sediment in the Delaware River

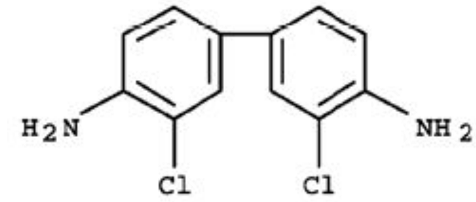


(Praipipat *et al.*, 2013 ES&T)

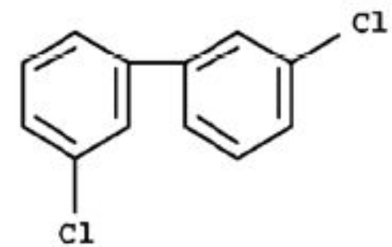
PCB 11 from Diarylide Yellows



Diarylide yellow



3,3’-dichlorobenzidine



PCB 11 (3,3’-diCB)

R_1,R_2,R_3 = H	Pigment yellow 12
R_1,R_2 = CH_3, R_3 = H	Pigment yellow 13
R_1 = OCH_3, R_2, R_3 = H	Pigment yellow 17
R_1,R_3 = OCH_3, R_2 = Cl	Pigment yellow 83

→ All listed in EPA’s Toxic Substances Control Act (TSCA) inventory

(Basu *et al.*, 2009)

Other PCBs in pigments

From Hu and Hornbuckle, 2010 ES&T

Simon Litten also found (dioxin-like) PCB 77 in pigment process waste, TEQ = 0.0001 (Litten *et al.*, 2002)

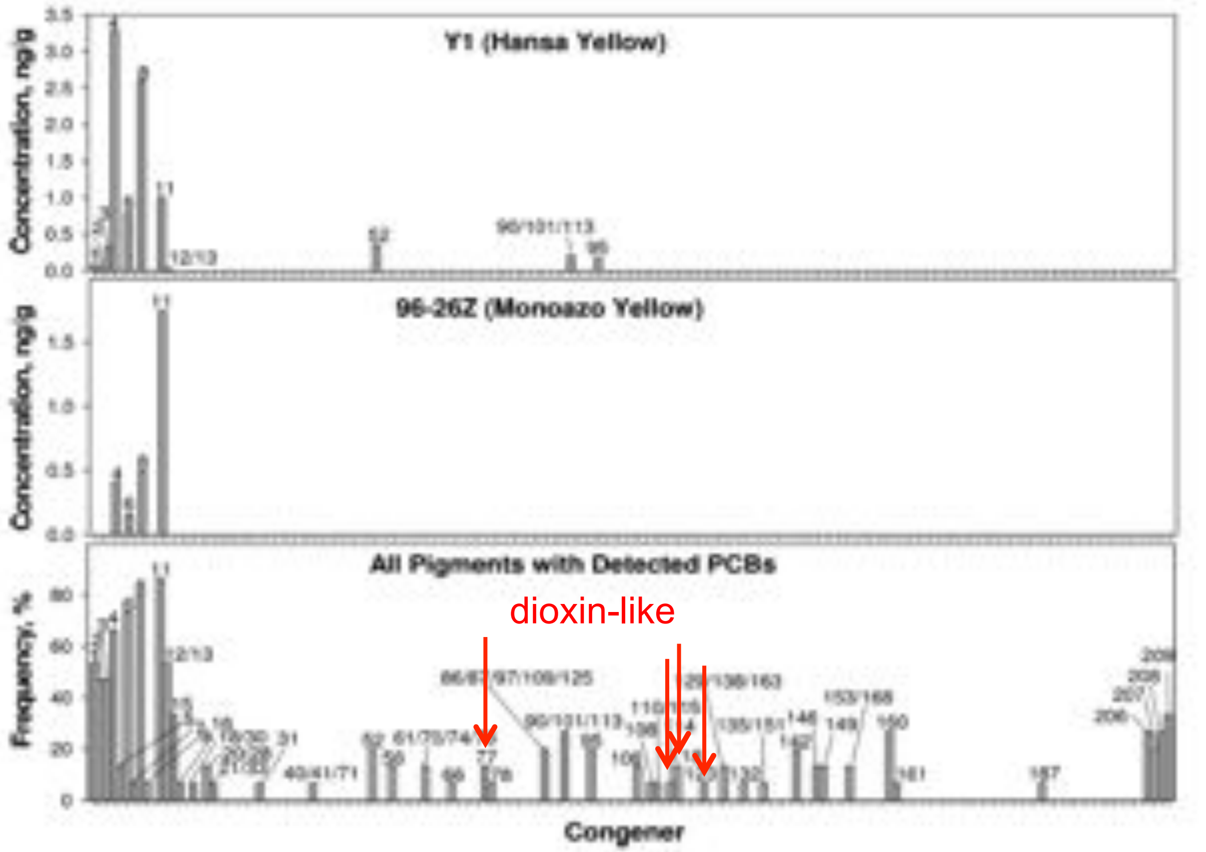
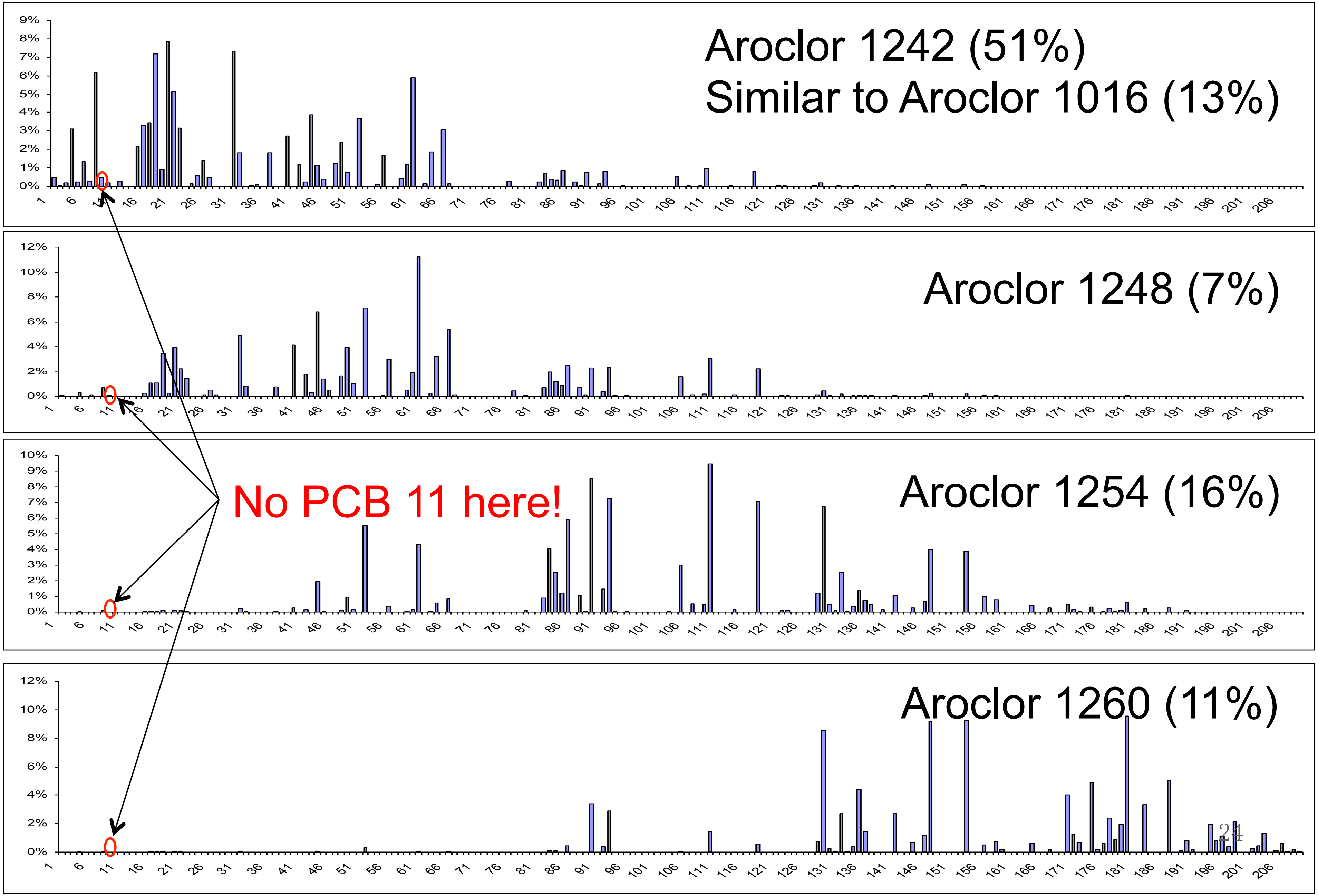


FIGURE 2. Examples of PCB profiles in paint pigments (top two plots) and the frequency of congener detection in the 15 pigments with detected PCBs (bottom plot).

Aroclors (% of US production)



TSCA contains a loophole allowing for inadvertent production of PCBs

Under TSCA, the inadvertent production of PCBs is allowed.

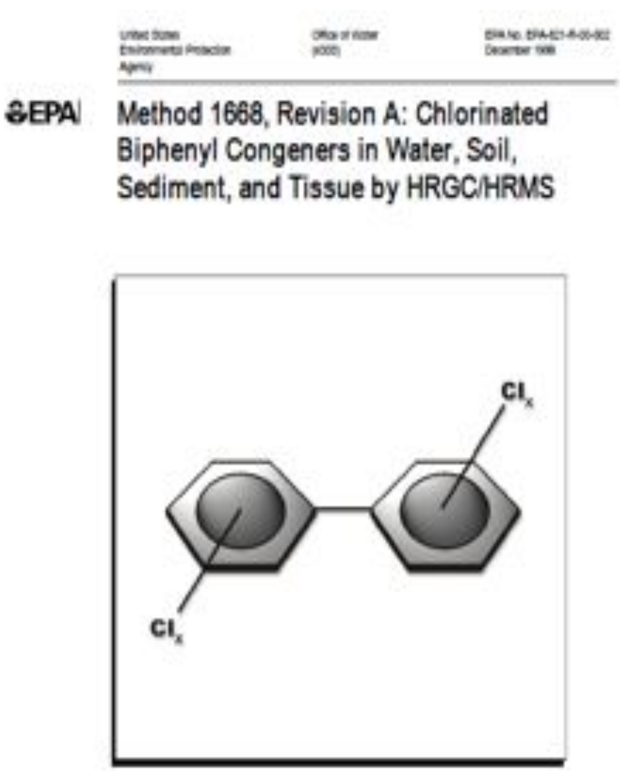
PCB concentrations in the product have to average less than 25 ppm and can be no higher than 50 ppm.

BUT, the concentrations of monochlorobiphenyls are divided by 10, and dichlorobiphenyls by 5.

(Pigment process waste is classified as hazardous waste)

Transfer of PCBs in a concentration of 50 mg/kg or over is prohibited by the Stockholm Convention on Persistent Organic Pollutants.

EPA method 1668A



EPA developed a new method to measure PCBs, using the new high-resolution GC/MS.

This method measured ALL of the PCB congeners, not just the ones in the Aroclors.

PCB 11 started showing up everywhere

Portland Harbor

San Francisco Bay

Santa Fe River

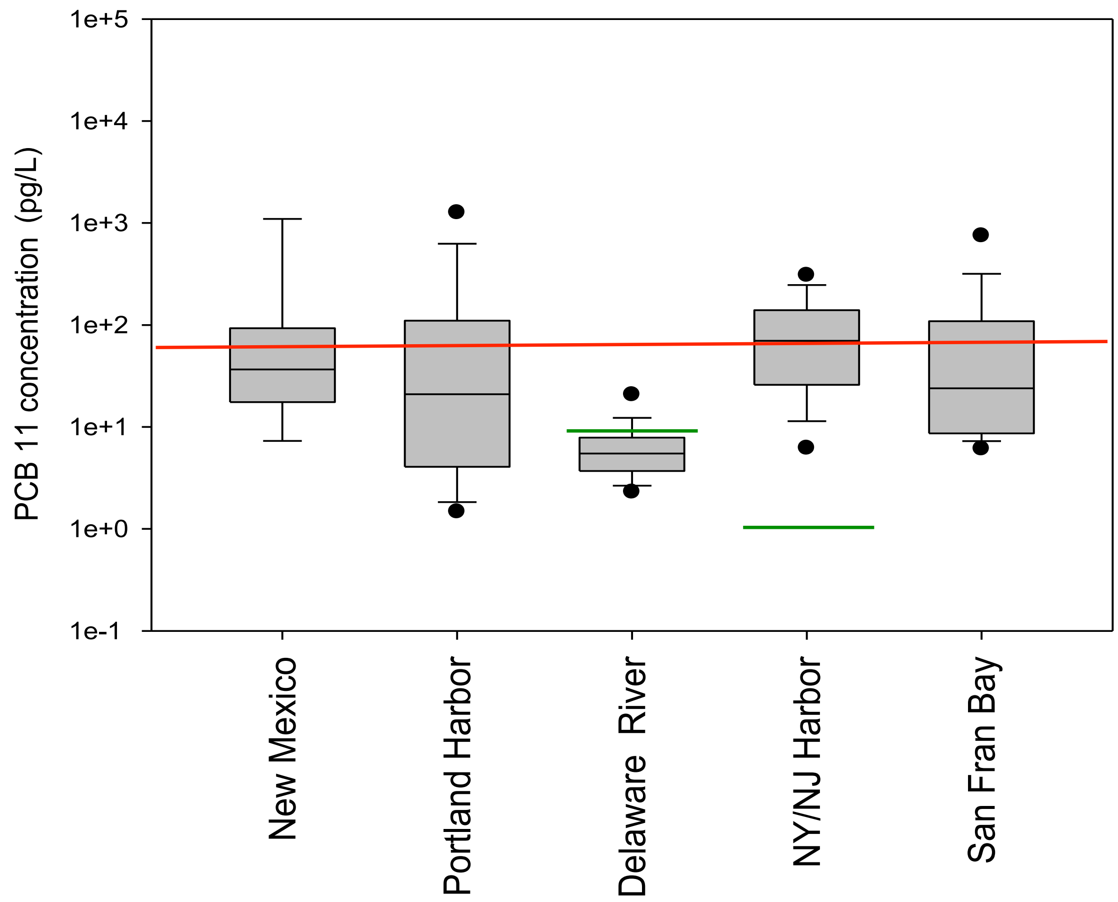
Rio Grande

Houston Ship Channel

NY/NJ Harbor

Delaware River

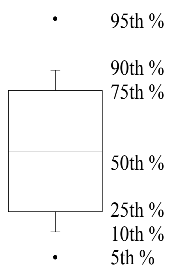
PCB 11 concentrations across US waterways



Water Quality Standards (WQS) ΣPCBs

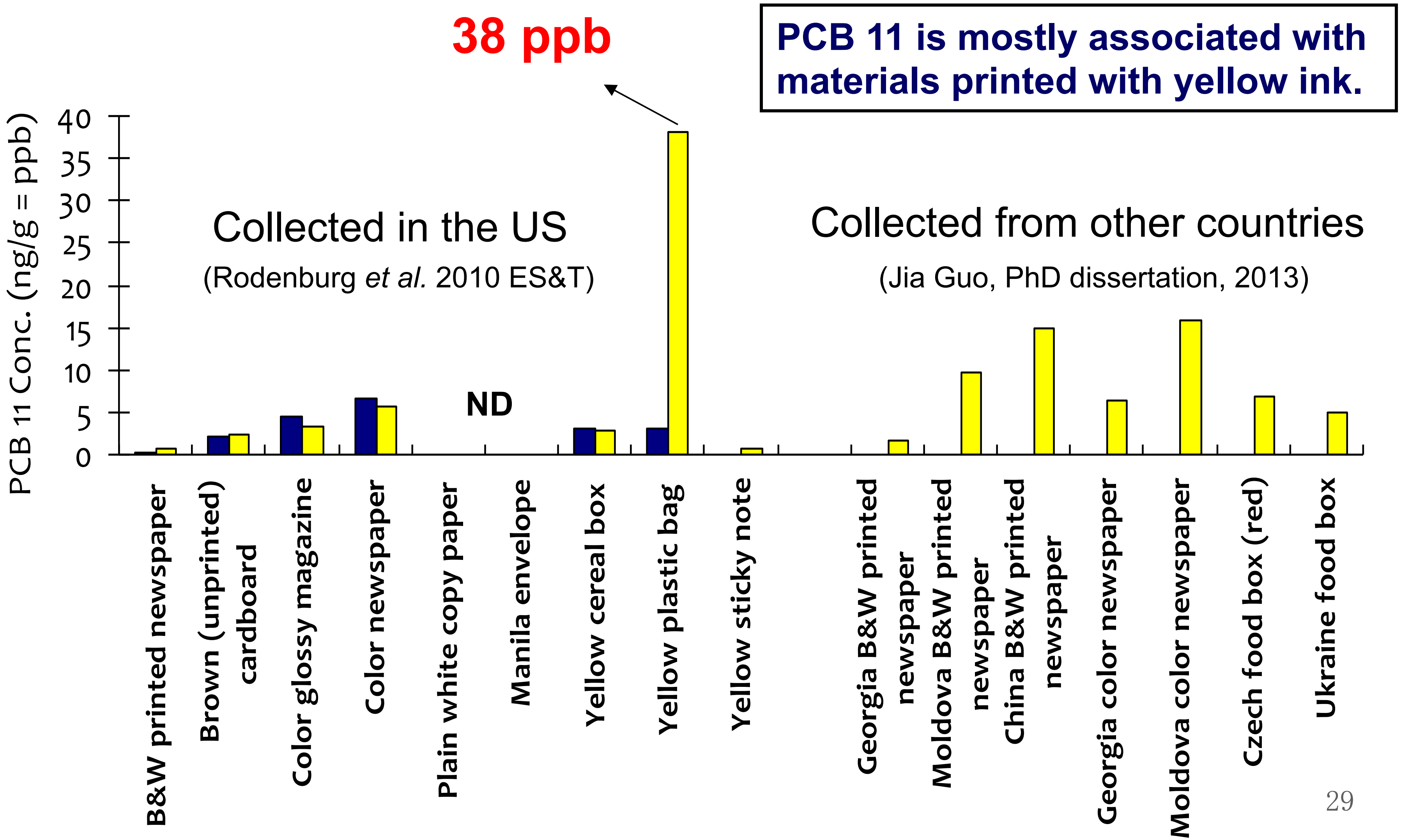
Federal WQS (64 pg/L)

Local WQS

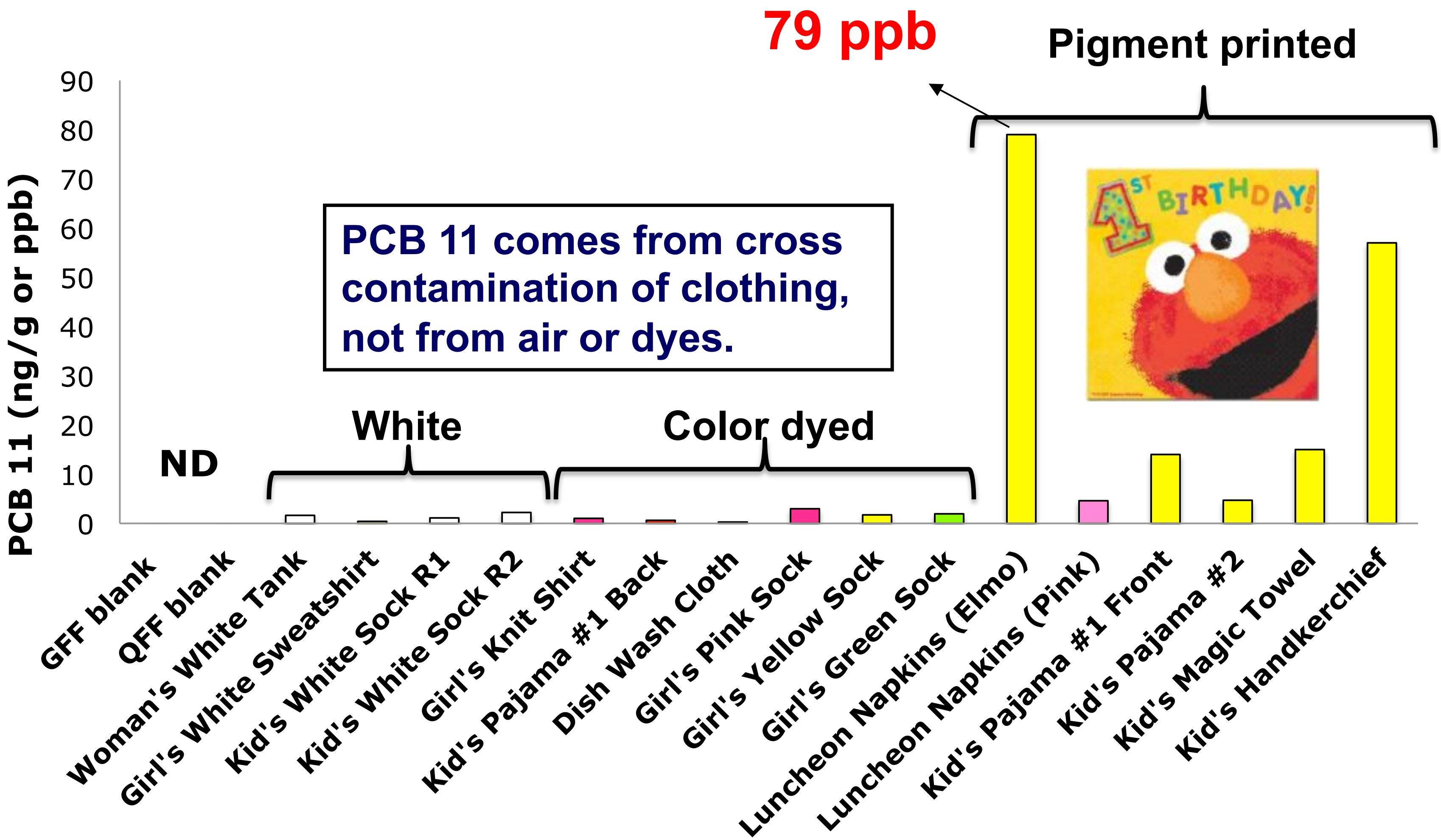


(Data from CARP, DRBC, SFEI, and STORET)

PCB 11 in Printed Materials

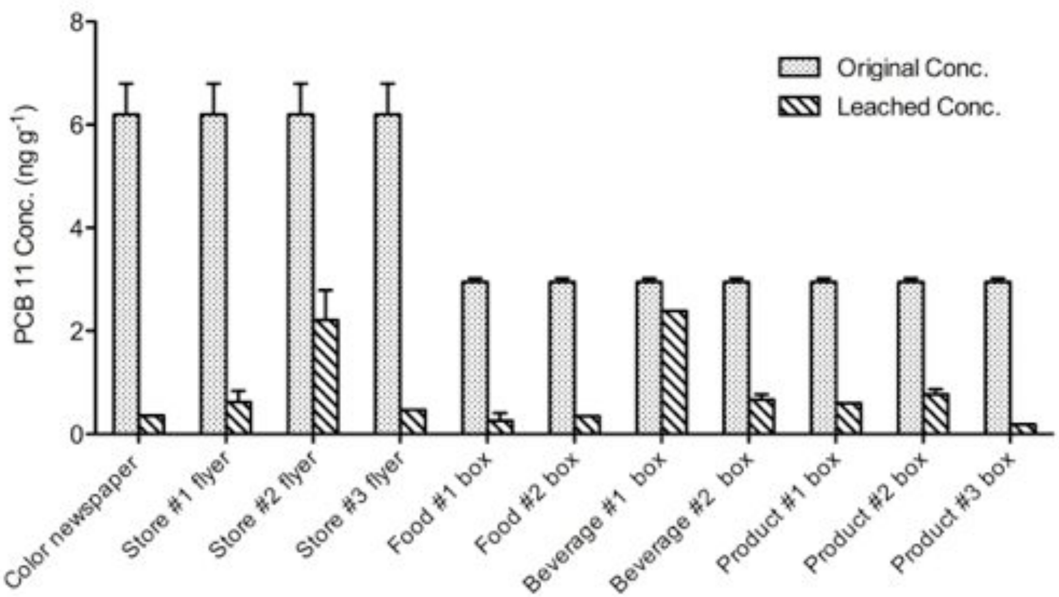


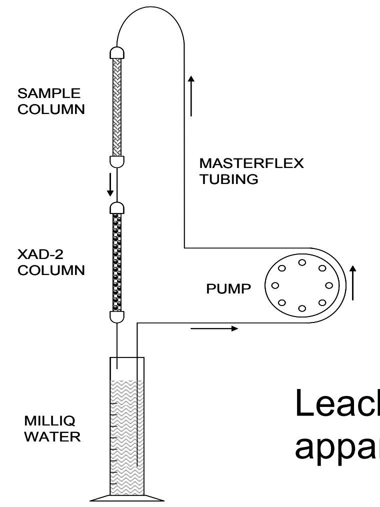
PCB 11 in Fabric Materials



(Jia Guo, PhD dissertation, 2013)

Leaching of PCB 11





Leaching apparatus

6~81% PCB 11 leached after 48 h

(Jia Guo, PhD dissertation, 2013)

A newspaper rapidly dissolving in front of my home

Pigment industry response

ETAD®

Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers

Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD), ETAD Position On The Presence Of Traces Of PCBs In Some Organic Pigments. **2011**.

"…PCBs are present both on the surface and in the solid pigment matrix. This incorporated PCB is unlikely to lead either to human or environmental exposure. Additionally pigments are used to colour paints, inks and plastics and are themselves incorporated into a further matrix making release improbable – until both polymeric matrix and the pigments degrade."

Mass flow analysis of PCB 11 in the Delaware River Basin (DRB)

$$\frac{\mathrm{dM}}{\mathrm{dt}} = I - O - R_{tot}$$

Accumulation = 0
@ steady state

Inflow

Outflow

Reaction

I>O: most PCB 11 stays in the pigment, only some gets out to environment

O>I: pigment degrades into PCB 11

(Jia Guo, PhD dissertation, 2013)

Total Maximum Daily Load (TMDL)

How much PCB 11 does pigment contain?

- Measured values range widely
  - PCB 11 in printing ink = 15 ng/g = 75 ng/g in pigment
  - Max allowed by law is average of 125 ppm (ug/g)
- Pigment production = 250,000 t (Savastano, 2007)
  - Range of 5 to 7,800 kg/y PCB 11 produced!
- Can 5 kg/y be reasonable?
- NO!
  - 40-100 kg/y of PCB 11 coming out of one WWTP that treats pigment process waste in the NYC area

How much PCB 11 enters the DRB each year?

- US consumes 20% of world pigment market (IHS, 2011)
- Assume pigment use scales by population
  - DRB = 2.7% of US population (2010 Census)

	PCB 11 in pigment	World PCB 11 production (kg/y)	PCB 11 Import to DRB (kg/y)
Low-end	75 ppb	5	**0.025**
High-end	125 ppm	7800	**42**

How much PCB 11 exits the DRB each year?

- Using the DRBC's excellent data set, we can calculate:
  - Flow of PCB 11 out to Atlantic (0.09 kg/y)
  - Sequestration in sewage sludge (0.28 kg/y)
  - Sequestration in river sediment (0.26 kg/y)

Lower bound estimate of 0.025 kg/y
into DRB is not reasonable!

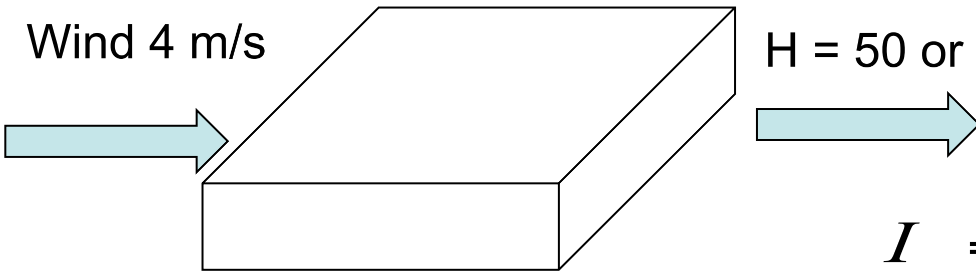
- Using our Delaware Atmospheric Deposition Network (DADN) data, we can calculate:
  - Volatilization to atmosphere

Air emissions required

Assume the DRB is a square:

Wind 4 m/s

H = 50 or 500 m (Diamond *et al.*, 2001)



W = L = 187 km

$$I = C_{ss} \cdot V \cdot (k_w + k_{tot})$$

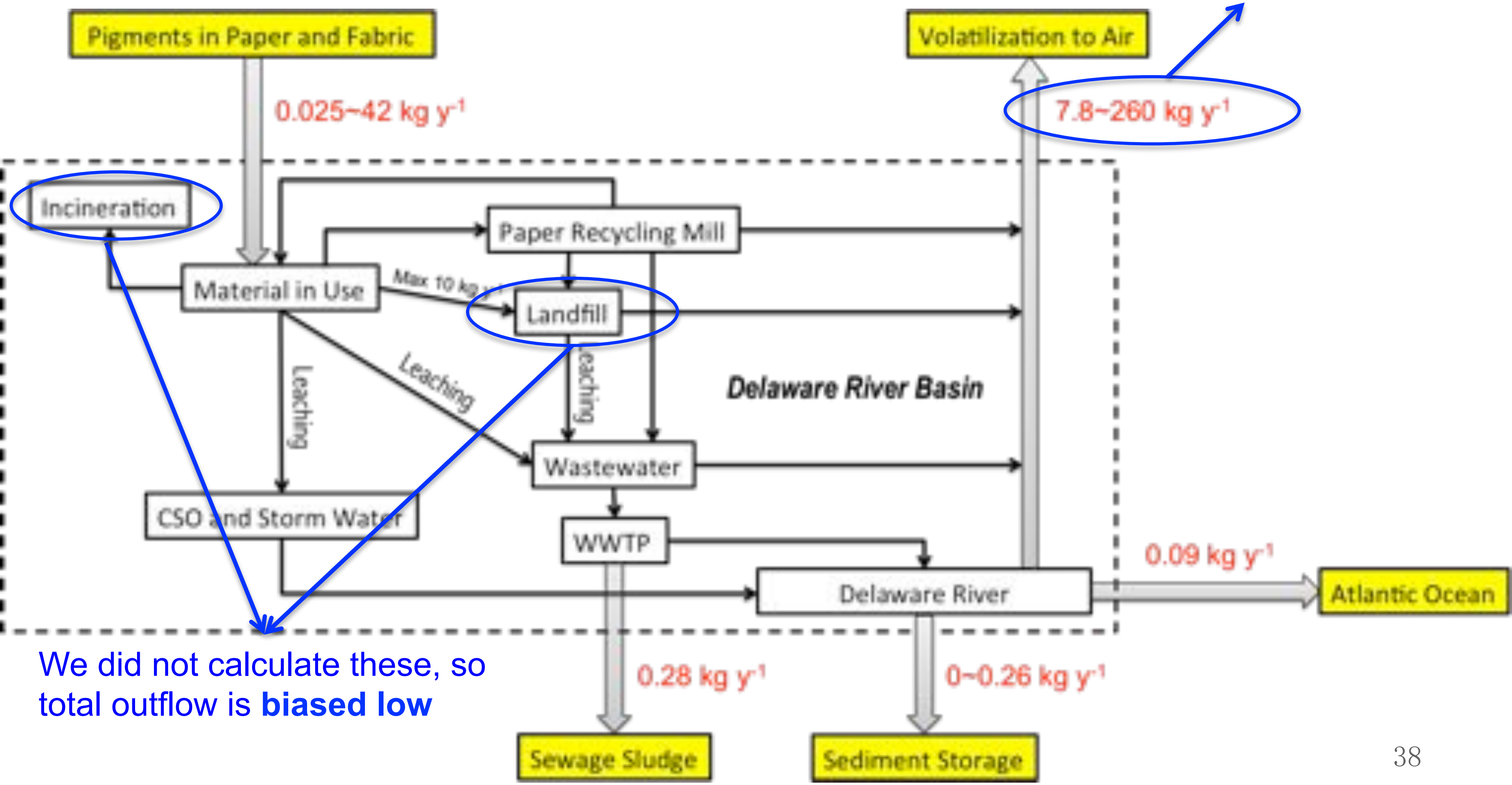
k_w = flushing rate = 1.85 1/d
k_{tot} = reaction with hydroxyl = 0.57 1/d

C_{ss} from DADN (pg/m^3)	H (m)	I (kg/y)
6	50	**7.8**
6	500	**78**
20	50	**26**
20	500	**260**

Similar to our top estimate of 42 kg/y into basin

Mass flows of PCB 11 in the DRB

Volatilization is the most important process — very uncertain!



We did not calculate these, so total outflow is **biased low**

No matter how you slice it…

- The lower bound estimate of PCB 11 in pigment can't be right
- The amount of PCB 11 in pigment must be close to the maximum allowed value of 125 ppm
- Virtually all of it gets out into the environment

- OR the concentration in the pigment is even higher than 125 ppm due to outsourcing of pigment production to other countries
- OR the pigment breaks down to release PCB 11
- OR we are missing some sources

Summary

- PCB 11 and other congeners from pigments significantly contribute to water pollution
- US WQS cannot be met until these sources are reduced or eliminated
- Human exposure via clothing, napkins, and printed material is possible
- PCBs enter the wastewater stream through disposal of paper and washing of clothing
- It is important to measure most or all of the 209 PCB congeners in monitoring programs

Environmental Council of States resolution

ECOS

- Recommends that U.S. EPA, industry, and states work together on alternatives to chlorinated solvents used in pigment and ink manufacturing to develop manufacturing processes in the next five years that do not generate PCBs, while making sure the alternatives do not themselves cause significant environmental impacts of their own;
- Supports a national approach to the problem of inadvertently-created PCBs and requests U.S. EPA commit research and development funds to establish the scope of the issue for all inadvertently-created PCBs and provide resources to establish a Design for the Environment project to reduce or eliminate inadvertently-created PCBs;
- Supports U.S. EPA's proposed rulemaking to reassess the current use authorizations for PCBs, which includes products with PCBs and products with inadvertently-generated PCBs. U.S. EPA should move forward with this rulemaking to better protect human health and the environment.
- Recommends that U.S. EPA continue its efforts to reduce PCBs and work with the international community on the elimination of PCBs.

Resolved 2012

Acknowledgements

HUDSON RIVER FOUNDATION
for Science & Environmental Research

new jersey department of environmental protection

Delaware River Basin Commission

Rutgers Office of Technology

NEW YORK STATE
DEPARTMENT OF ENVIRONMENTAL CONSERVATION

RUTGERS
New Jersey Agricultural Experiment Station

E S
Environmental Sciences
Rutgers University

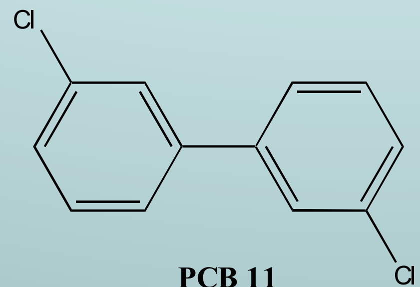
Alternatives for elimination of polychlorinated biphenyls (PCBs) in pigments used for printing inks and architectural paints.

Professor R M Christie

Heriot-Watt University, Scotland, UK
King Abdulaziz University, Saudi Arabia

PCBs in Pigments

- PCBs may be unintentionally generated during the manufacture of certain organic pigments (ETAD position on the presence of traces of PCBs in some organic pigments, 2010)
- L.A. Rodenburg, J. Guo, S. Du & G. J. Cavallo, *Evidence for the unique and ubiquitous environmental sources of 3,3'-dichlorobiphenyl*, Environ. Sci, Technol, 2010, **44**, 2816-2821



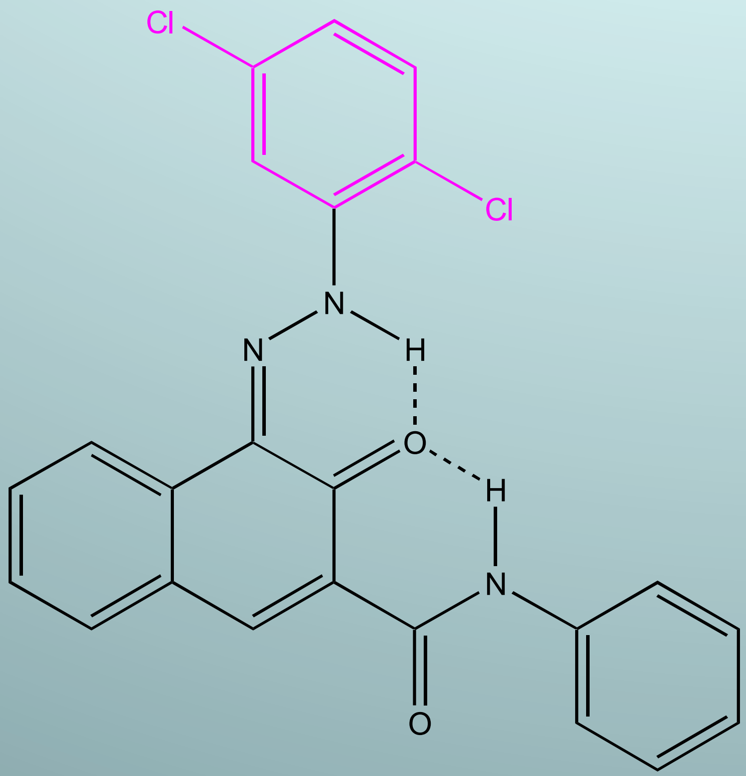
PCB 11

- D. Hu and K.C. Hornbuckle, *Inadvertent polychlorinated biphenyls in commercial paint pigments*, Environ. Sci. Technol., 2010, **44**, 2822-2827
  - levels of PCBs in certain azo and copper phthalocyanine pigments identified
- Ministry of Economy, Trade and Industry (METI), Japan, *Compiled results of re-analysis of the presence of polychlorinated biphenyls (PCBs) as by-products in organic pigments*, May 2013
  - 2 structural groups of azo pigments implicated
- ***There is a need for wider investigation for clarification / verification***

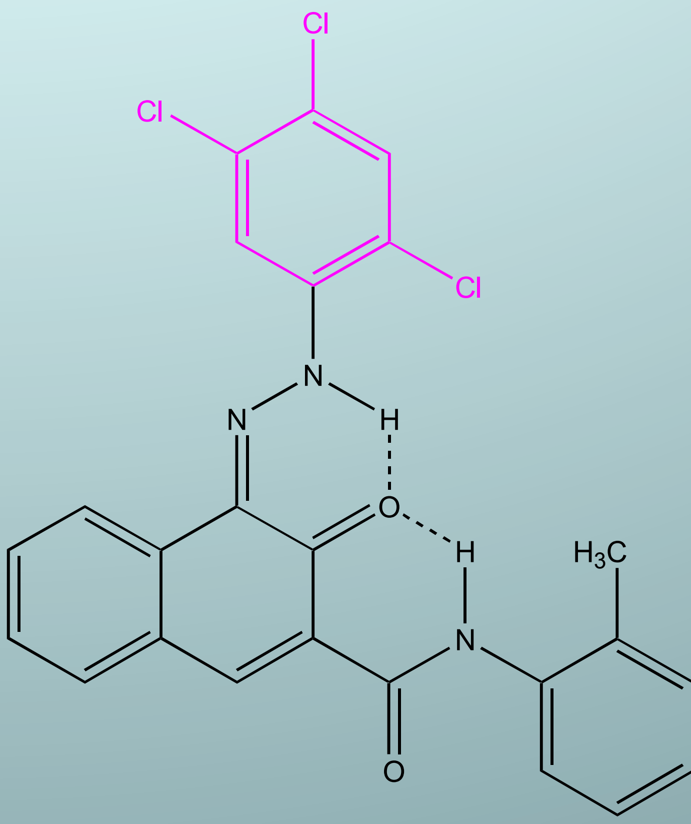
METI Report, May 2013

Pigment name	Brand name	Measurements were reported
Pigment Red 2	ZA-855 Red	37～58ppm
Pigment Red 112	· ZA-862 Red Permanent Red GY	16-121ppm
Pigment Red 2	PERMANENT RED G-87	52ppm
α-(2,5- dichlorophenyl azo)-2-α-acetyl acetamide-6-ethoxy benzothiazole (generic name: Pigment Yellow -165)	FAST YELLOW F5G	208ppm
Pigment Yellow 13	· DISAZO YELLOW3GR-M · DISAZO YELLOW3GR-M-5	220ppm
Pigment Yellow 83	· SUMIKAPRINT FASTYELLOW HR-M · SUMITONE FASTYELLOW HR-M-5 ·SUMIKAPRINT FASTYELLOW HR-T-2 · SUMIKAPRINT FASTYELLOW HR-SP · PY-2GN	52～280ppm
Pigment Red 2	FAST RED F2R (PR-2) POWDER	61 ppm
Pigment Yellow 12	Pigment Yellow1207	1500 ppm
Pigment Orange 13	Orange BO-01	1,000ppm
Pigment Yellow 55	･SUIMEI YELLOWDRO-1 SYMULER FastYellow 4539	1,500ppm
Pigment Yellow 14	SUIMEI YELLOWGGNB	810ppm
Pigment Yellow 17	SUIMEI YELLOW7G SUIMEI YELLOW7GKT	1000 ppm 700 ppm
Pigment Yellow 83	･SUIMEI YELLOW ERT ･SUIMEI YELLOW 5RT	2,000 ppm
Pigment Orange 34	SUIMEI PYRAZOLONEORANGE GR-N	190 ppm
Pigment Yellow 81	SUIMEI YELLOWF10G	79 ppm
Pigment Yellow 12	Disazo Yellow G178－4	110 ppm
Pigment Yellow 83	Permanent YellowHR-1183-2	59 ppm

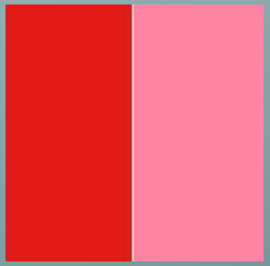
Monoazo pigments derived from dichloro- and trichloroanilines



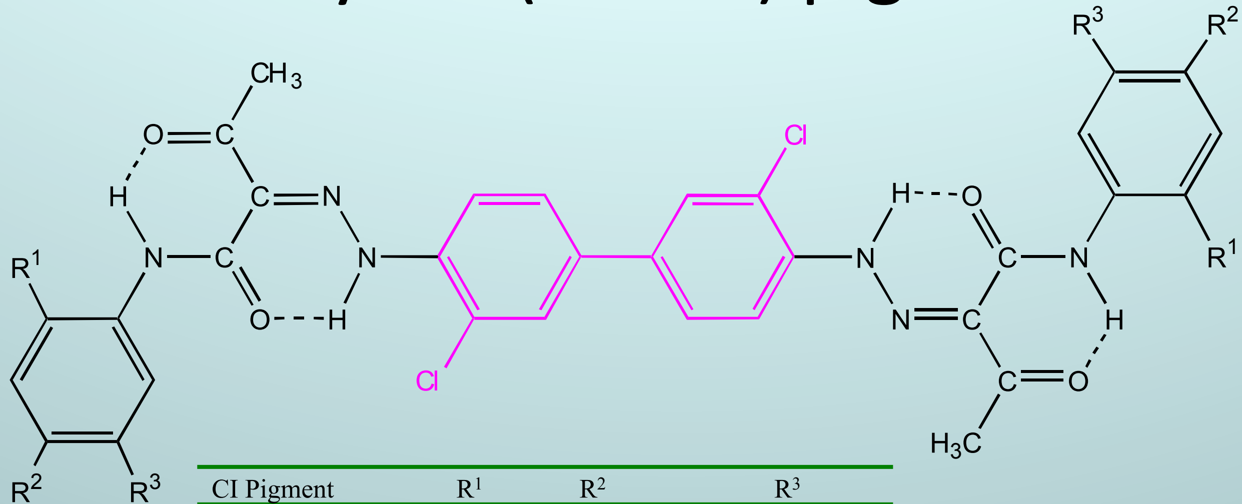
CI Pigment Red 2



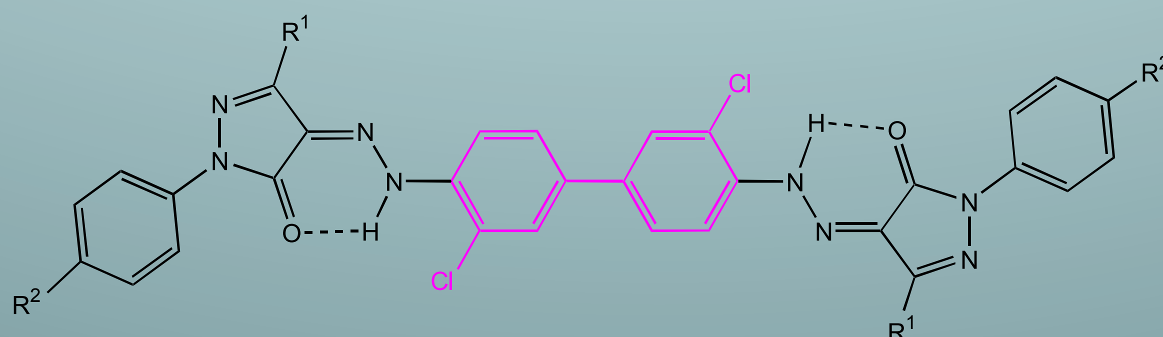
CI Pigment Red 112



Diarylide (disazo) pigments



CI Pigment	R^1	R^2	R^3
Y12	H	H	H
Y13	CH_3	CH_3	H
Y14	CH_3	H	H
Y17	OCH_3	H	H
Y55	H	CH_3	H
Y83	OCH_3	Cl	OCH_3



CI Pigment	R^1	R^2
Orange 13	CH_3	H
Orange 34	CH_3	CH_3

Alternatives?

- Address any *confirmed* issues in current products

- Substitute with ‘PCB-free’ products

  - (a) from current product ranges
  - (b) with new products

'PCB-free'

- a misleading term?
- Is it feasible to assert that there is a ***zero*** level in a particular product under all circumstances?
- "The pigments most likely to show trace PCB contamination are those that
  – contain **chlorine** as part of their molecular structure
  – use **chlorine**-containing raw materials
  – use **chlorine**-containing aromatic solvents in their synthesis."

Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD), January 2011

- On this basis, *inorganic pigments* and *azo pigments not containing chlorine*, eg., CI Pigment Yellow 1, are probably *potentially* 'PCB free'
- Alternatively, assess on the basis of the 'mechanistic potential' to form PCBs

Manufacture of azo pigments

$$\text{Ar-NH}_2 \xrightarrow[\text{diazotisation}]{\text{NaNO}_2\text{ / HCl}} \text{Ar-N}_2^+ \xrightarrow[\text{azo coupling}]{\text{Ar'-H}} \text{Ar-N=N-Ar'}$$

monoazo pigment

$$\text{H}_2\text{N-Ar-NH}_2 \xrightarrow[\text{tetrazotisation}]{\text{2 NaNO}_2\text{ / HCl}} {}^+\text{N}_2\text{-Ar-N}_2^+ \xrightarrow[\text{azo coupling}]{\text{2 Ar'-H}} \text{Ar-N=N-Ar'-N=N-Ar}$$

disazo (diarylide) pigment

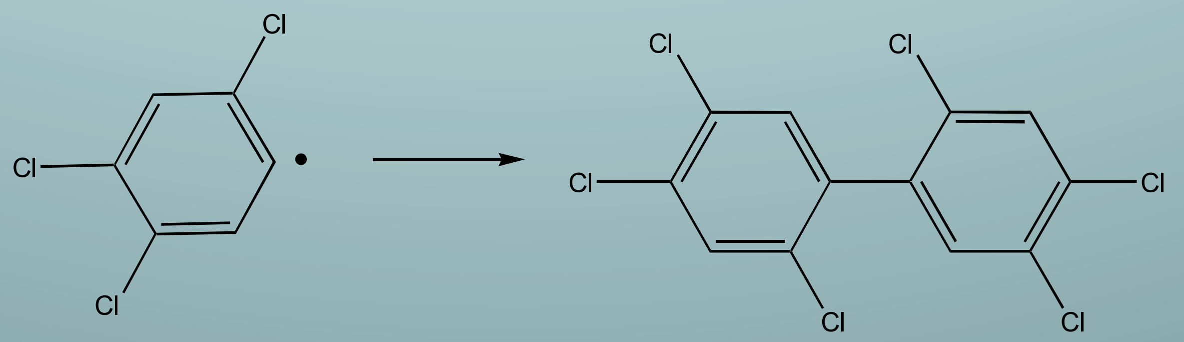
- in water as solvent
- under controlled conditions to minimise impurity formation

Inadvertent PCB formation in monoazo pigment manufacture – a hypothesis

(a) $$Ar\text{-}N_2^{+} \xrightarrow[\text{electron transfer}]{\text{homolytic dediazoniation,}} \underset{\text{aryl radical}}{Ar^{\cdot}} + N_2$$

(b) $$2\ Ar^{\cdot} \longrightarrow Ar\text{-}Ar$$

e.g., 2



•H. Zollinger, *Diazo chemistry I*, VCH, Weinheim, 1994.

• C.Galli, *Radical reactions of arenediazonium Ions: an easy entry into the chemistry of the aryl radical*, Chem. Rev., 1988, 88, 765.

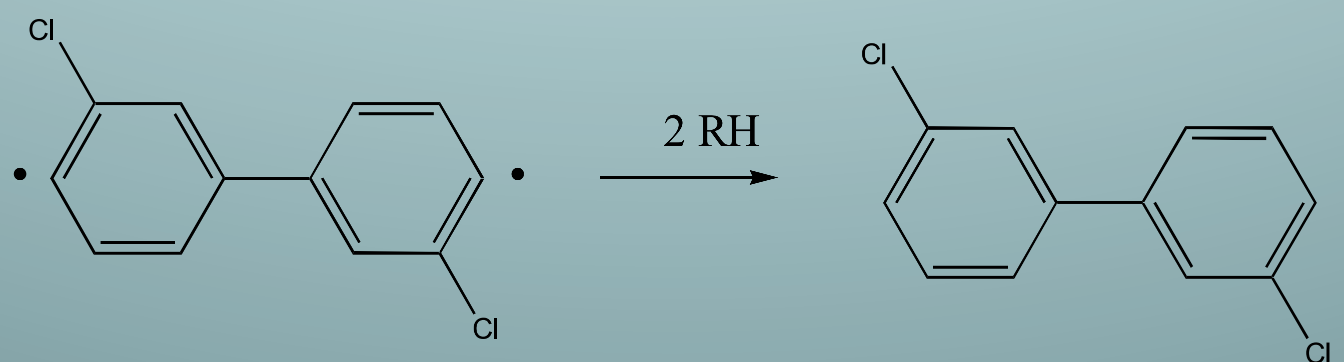
Inadvertent PCB formation in diarylide (disazo) pigment manufacture – a hypothesis

(a) $Ar\text{-}N_2^+ \xrightarrow[\text{electron transfer}]{\text{homolytic dediazoniation,}} Ar^{\cdot} + N_2$

aryl radical

(b) $Ar^{\cdot} + RH \xrightarrow{\text{hydrogen abstraction}} ArH$

e.g.,



PCB 11

Potential approaches to minimise PCB formation in azo pigment manufacture

- Test hypothesis by experimental investigation (or propose others).
- Devise methods to eliminate free radical formation and reactions

Potential Alternatives for Yellow 165, Red 2, Red 112

- ***Yellow 165***, low usage (Japan only)

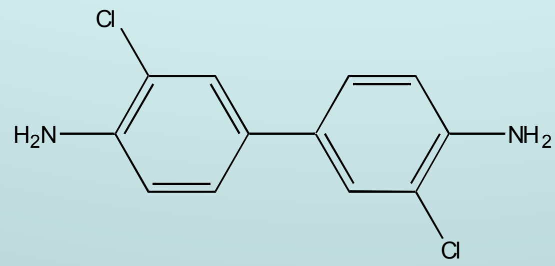
- ***Red 2***, printing inks
- ***Red 112***, printing inks, paints plastics
- There is no potential for substitution of red organics by inorganic pigments
- Higher performing azo pigments (Red 170, etc.), high performance organics (at higher cost!)?

•W. Herbst & K. Hunger, *Industrial Organic Pigments*. *Production, Properties, Applications*, 3rd edition, Wiley-VCH, Weinheim, 2004.
•G. Buxbaum & G. Pfaff (eds.), *Industrial Inorganic Pigments*, *Production, Properties, Applications,* 3rd edition, Wiley-VCH,Weinheim, 2005.

Potential Alternatives for Diarylide pigments

- These are high volume printing ink pigments providing the yellow process colour, especially ***Y12, Y13, Y14***.
- They provide high colour strength and brightness, and high transparency at low cost
- There are ***no*** obvious substitutes for printing ink applications in the current commercial range
- A few pigments are suitable for application in architectural paints (notably ***Y83***)
- There are potential alternatives for paints, e.g., from the range of monoazo pigments, high performance organics and a few inorganics (bismuth vanadate?)

Potential Alternatives for Diarylide pigments

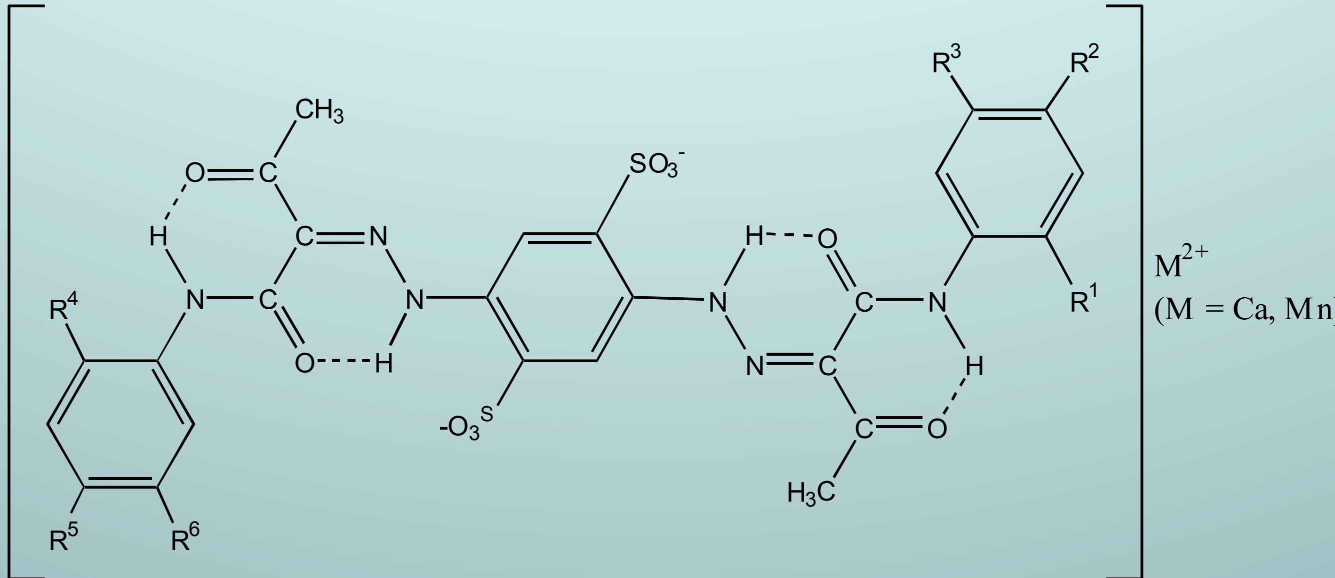


- Previous exploration of this issue has been based on the toxicity of the starting material - 3,3’-dichlorobenzidine (DCB)
- Requires strict industrial handling procedures
- The pigments are non-toxic but there is evidence for thermal degradation of the pigments to generate DCB in applications involving high temperatures, e.g., in thermoplastics

  – B. Az, R. Dewald & D. Schnaitmann, *Pigment decomposition in polymers in applications at elevated temperatures*, Dyes & Pigments, 1991, 15, 1.

- Substitutes for these applications have been found, e.g., specific monoazos, high performance organics, and inorganics.

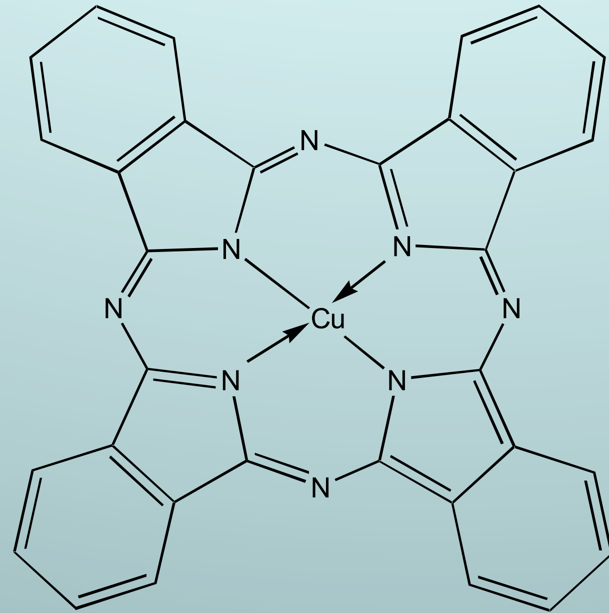
Potential Alternatives for Diarylide pigments



- R. M. Christie & B. D. Howie, *Potential alternatives for 3,3'-dichlorobenzidine as tetrazo components for diarylide yellow and orange pigments: Part 1: p-phenylenediamine and its derivatives*, Dyes & Pigments, 2009, 80, 245-253.

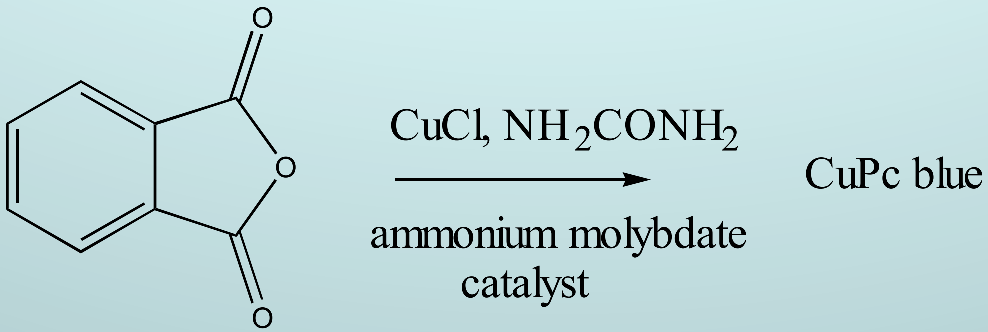
- May offer possible potential for long term approach to new products

Copper phthalocyanine



- 'the perfect blue pigment'
- suitable for most pigment applications
- a 'chlorine-free' product
- little historical demand for alternatives
- not apparently implicated in Japanese study

Synthesis of CuPc



- Requires high temperatures
- Source of PCB is proposed as pyrolysis of dichloro- and trichlorobenzene used as reaction solvent
  - D. Hu and K.C. Hornbuckle, *Inadvertent polychlorinated biphenyls in commercial paint pigments*, Environ. Sci. Technol., 2010, 44, 2822-2827
  - P.Y.Liu, M.H.Zheng, B. Zhang & X.B. Xu, *Mechanism of PCB formation from the pyrolysis of chlorobenzenes*, Chemosphere, 2001, 43, 783-785.
- Free radical mechanisms are invoked
- There is potential to minimise using chlorine-free solvents (SBS Pigments, India) or solvent-free 'dry-bake' processes

Copper phthalocyanine green

- Polychlorinated copper phthalocyanine, CI Pigment Green 7
- Synthesis involves CuPc treated with chlorine in $AlCl_3$/NaCl melt
- High congener PCBs have been identified in a product
  - D. Hu and K.C. Hornbuckle, *Inadvertent polychlorinated biphenyls in commercial paint pigments*, Environ. Sci. Technol., 2010, 44, 2822-2827
- Potential mechanisms of formation of PCBs are less obvious and require to be established
- Alternative green pigments include chromium oxide, CI Pigment Green 1 (basic dye complex pigment), although neither are comparable products
- There has been recent patent activity towards halogen-free green pigments

- BASF Heliogen copper phthalocyanine pigments report
  - < 2ppm in copper phthalocyanine blue
  - 2-25 ppm in copper phthalocyanine green

Concluding remarks

- Azo and CuPc pigment manufacture in recent decades has transferred substantially (not completely) from USA, Europe and Japan, to China and India. Western users of these pigments now rely heavily on imported products.
- ***There is a need for clarification / verification of the issues***
- ***Challenges become opportunities ?***

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